Chapter I

Introduction

Fischer-Tropsch synthesis is a route for producing liquid fuels from synthesis gas, a mixture of CO and H_2 (1-3). The most attractive potential sources of synthesis gas are the steam reforming of natural gas (methane) and the gasification of coal. Natural gas is often found in remote locations, and conversion to liquid fuel would facilitate storage, transportation and utilization of this resource. Further, since coal is much more abundant than the natural reserves of liquid hydrocarbons, considerable interest in hydrocarbon synthesis from CO and H_2 has been generated by the need for long-range alternative sources of liquid fuels.

The composition of the products of Fischer-Tropsch synthesis depends on the catalyst employed as well as the reaction conditions, in particular, the pressure, the temperature, and the H_2/CO ratio. The predominant products of Fischer-Tropsch synthesis are linear alkanes and alkenes as well as H_2O or CO_2. Aldehydes, alcohols, and carboxylic acids are also formed, but in lower concentrations than hydrocarbons.

The group VIII metals Fe, Co and Ru are active for Fischer-Tropsch catalysis. Promoters and supports can also influence the activity and selectivity of a catalyst. Since a broad product distribution of hydrocarbons, ranging from methane to heavy waxes is produced, it is desirable to enhance the selectivity for liquid hydrocarbons. In order to accomplish this goal, research efforts are directed towards a better understanding of the mechanism of the reaction and the elementary surface processes involved in the reaction.

The reaction mechanism can be viewed as a surface polymerization process in which the monomer is produced *in situ* from CO and H_2 on the catalyst surface (2). The products of the reaction often follow an Anderson-Schulz-Flory (ASF) distribution, for which $[C_{n+1}]/[C_n] = \alpha$, where α is independent of chain length, n, and $\alpha < 1$. If it is assumed that polymerization occurs via the addition of a C_1 monomer unit to growing hydrocarbon chains, then α represents the probability of chain growth and is given by $\alpha = r_p/(r_p+r_t)$, where r_p and r_t are the rates of chain propagation and chain termination, respectively. Although the effects of process variables such as reaction temperature and H_2/CO ratio on the product distribution (i. e., α) and overall activity have been well-studied, the elementary reaction steps that occur during the reaction are not well-understood.

The objective of the present investigation is to better understand the elementary steps that constitute the CO hydrogenation reaction. One goal is to characterize catalyst deactivation and to try and understand the causes of catalyst decay. Isotopic tracers and temperature-programmed surface reaction (4) are used for this purpose. A second goal is to elucidate the mechanism of chain growth during Fischer-Tropsch synthesis. In particular, it is desirable to obtain the rate constants for chain initiation, propagation and termination and to determine surface coverages by reaction intermediates. Isotopic tracers are combined with transient-response experiments in order to accomplish this aim, since steady-state rate data can only yield product formation rates and distributions (5, 6). Finally, the effect of ethylene addition to the CO/H_2 Fischer-Tropsch synthesis feed on chain initiation and propagation is investigated. Isotopic labelling is used to differentiate between carbon from CO and carbon from ethylene in the product. This further allows the dynamics of ethylene incorporation to be studied.

Ruthenium supported on titania is used in this work for several reasons. Ruthenium has a high specific activity for Fischer-Tropsch synthesis and has high chain growth probabilities at mild reaction conditions (7). A ruthenium catalyst produces mainly straight-chain hydrocarbons, which are believed to be the primary reaction products. Ruthenium does not produce large amounts of oxygenates, thereby simplifying product identification and analysis. Titania is used to support and disperse the ruthenium since titania-supported Group VIII metals are known to be more active than silica- or alumina-supported Group VIII metals (8-11).

This thesis is divided into four parts. Chapter 2 is a study of catalyst deactivation during CO hydrogenation. The dynamics of catalyst deactivation are determined and the role of the build up of carbonaceous species is assessed. The effects of Ru dispersion, TiO_2 phase and TiO_2 surface area on catalyst activity and selectivity are determined. In Chapter 3, expressions are derived for evaluating the rate coefficients for chain propagation, k_p, and for chain termination, k_t. Chapter 4 describes the use of the isotopic transient technique to evaluate the rate coefficients for chain initiation, propagation, and termination, and the coverages by reaction intermediates. The effects of reaction temperature and the D_2/CO ratio in the feed on rate coefficients and surface coverages are investigated. Chapter 5 describes the effect on chain growth of adding small amounts of ethylene to the CO/H_2 feed.

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